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Comparison of *in-situ* and *ex-situ* catalytic pyrolysis in a micro-reactor system



Kaige Wang^{a,b}, Patrick A. Johnston^a, Robert C. Brown^{a,b,*}

^a Center for Sustainable Environmental Technologies, Iowa State University, Ames, IA 50011, United States

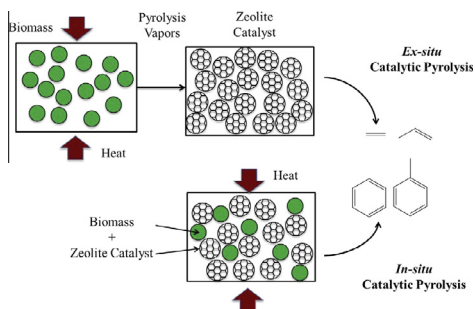
^b Department of Mechanical Engineering, Iowa State University, Ames, IA 50011, United States

HIGHLIGHTS

- *Ex-situ* and *in-situ* catalytic pyrolysis were compared in a micro-reactor system.
- *Ex-situ* catalytic pyrolysis produced significantly more olefins than *in-situ*.
- A dual catalytic cycle reaction mechanism is proposed.

GRAPHICAL ABSTRACT

Aromatics vs. olefins from catalytic pyrolysis: *in-situ* and *ex-situ* catalytic pyrolysis were compared in a micro-reactor system. *Ex-situ* catalytic pyrolysis produced significantly more olefins while *in-situ* produced more aromatics. A dual catalytic cycle reaction mechanism is proposed based on the experimental results.



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ABSTRACT

In this study, we compared *ex-situ* catalytic pyrolysis (CP) and *in-situ* CP of hybrid poplar in a micro-reactor system. When both pyrolysis and catalysis were performed at 700 °C, the carbon yield of olefins was greater for *ex-situ* CP than for *in-situ* CP (17.4% vs. 5.4%). On the other hand, *in-situ* CP produced more aromatic hydrocarbons than *ex-situ* CP (26.1% vs. 18.9%). The remarkably high yield of olefins from *ex-situ* CP indicates the potential of exploiting the process to preferentially produce olefins as a primary product from biomass, with aromatics being the secondary products. The carbon yield of carbonaceous residues from *ex-situ* CP was 18.6% compared to 31.3% for *in-situ* CP. Substantial carbon was deposited as char during *ex-situ* CP, which could be easily recovered as by-product, simplifying catalyst regeneration. The effects of catalyst loading, pyrolysis temperature and catalysis temperature on product distributions for *ex-situ* CP were also investigated. Our results showed that catalyst temperature strongly affected product distribution. While high catalyst temperature enhanced both olefin and aromatic production, yield of olefin increased to a greater extent than did aromatics. Neither pyrolysis temperature nor catalyst loadings had significant effect on product distribution for *ex-situ* CP.

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* Corresponding author at: Iowa State University, 1140E Biorenewables Research Lab, Ames, IA 50011, United States. Tel.: +1 515 294 7934; fax: +1 515 294 3091.

E-mail address: rcbrown3@iastate.edu (R.C. Brown).

1. Introduction

Fast pyrolysis has emerged as a promising technology for the production of biofuels and biobased products. The resulting bio-oil is a complex mixture of oxygenated compounds, including carboxylic acids, aldehydes, ketones, sugars, furans and phenolic compounds (Huber et al., 2006). The high oxygen content and instability during storage of bio-oil impedes commercial deployment of pyrolysis technology. Catalytic pyrolysis has emerged as a means for improving the quality of liquid products from pyrolysis (Carlson et al., 2010, 2009; Iliopoulou et al., 2014; Marker et al., 2012; Venkatakrishnan et al., 2014). Although alkali in biomass can catalytically react with solid biomass (Patwardhan et al., 2011, 2010), most heterogeneous catalysts appear to react with the vapor products released from pyrolyzing biomass (Carlson et al., 2010, 2009; Mihalcik et al., 2011; Zhang et al., 2012).

Depending upon the method of contacting catalyst and pyrolysis vapors, the process is classified as either *in-situ* or *ex-situ* catalytic pyrolysis. For *in-situ* catalytic pyrolysis (*in-situ* CP), the catalyst is mixed with the biomass to be pyrolyzed. For *ex-situ* catalytic pyrolysis (*ex-situ* CP), biomass is separately pyrolyzed and the resulting vapor products are transported to a catalysts bed downstream of the pyrolyzer. Catalytic pyrolysis can be performed in the presence of transition metal or precious metal catalysts and gaseous hydrogen to promote hydrodeoxygenation, in which case the process is referred to as hydropyrolysis (Marker et al., 2012; Venkatakrishnan et al., 2014). Otherwise, zeolite catalysts such as HZSM-5 are used to deoxygenate pyrolysis vapors through decarbonylation, decarboxylation and dehydration to produce aromatics and olefins (Carlson et al., 2009; Wang et al., 2014; Zhang et al., 2012). Catalytic pyrolysis with zeolites is attractive for several reasons. Zeolites are relatively inexpensive and robust compared to transition metal and precious metal catalysts. They can be readily regenerated to remove deposits of coke. They do not require hydrogen or other reactive agents and can be used at atmospheric pressure. Thus, zeolites are very attractive for both *in-situ* and *ex-situ* catalytic conversion of pyrolysis vapors into partially or fully deoxygenated molecules suitable as blendstocks for refining to hydrocarbon transportation fuels.

In-situ CP using zeolites has been conducted in both continuous and batch reactors. Aho et al. (2008) investigated catalytic pyrolysis in a fluidized bed reactor with zeolite catalyst as bed materials. Their result found that HZSM-5 zeolite gave the highest yield of organic fraction in bio-oil compared with other types of zeolites. The organic fraction was not fully deoxygenated and contained aldehydes, acids, ketones, phenols and other oxygenates. More recently, Huber's group reported *in-situ* CP in a fluidized bed reactor using HZSM5 catalyst to produce aromatic hydrocarbons (Carlson et al., 2011; Cheng et al., 2012; Zhang et al., 2012). Carbon yield of aromatic hydrocarbons was 23.2% when gallium was added to H-ZSM5 and pyrolyzed in continuous fluidized bed reactor (Cheng et al., 2012). Other researchers have reported partial deoxygenation rather than complete deoxygenation for *in-situ* CP experiments in fluidized bed reactors (Aho et al., 2008; Iliopoulou et al., 2014; Williams and Nugranad, 2000; Zhang et al., 2009). Zhang et al. (2009) performed catalytic pyrolysis of corncobs in a fluidized bed reactor in the presence of HZSM-5 zeolite and found the oxygen content of the bio-oil to decrease. Recently, Py-GC/MS, which closely couples an analytical pyrolyzer to a GC/MS, has been widely used to investigate catalytic pyrolysis because it makes possible rapid on-line characterization of pyrolysis products. Extensive studies of *in-situ* CP have been conducted on this type of microgram-scale reactor to explore the complex reaction mechanism of CP (Carlson et al., 2010, 2009; Foster et al., 2012; Mihalcik et al., 2011; Wang and Brown, 2013).

Although Py-GC/MS is a powerful analytical tool for non-catalytic and *in-situ* CP research, it does not lend itself to studies of *ex-situ* CP because of the absence of a second furnace to contain the catalyst bed. Even though *ex-situ* CP can be performed by separating the catalyst and biomass by quartz wool in the micro-reactor of Py-GC/MS (Lu et al., 2010; Zhang et al., 2014), this does not allow independent control of pyrolysis and catalysis reaction conditions. *Ex-situ* CP in the past was mostly conducted using bench-scale continuous reactors. Evans Robert and Milne (1988) reported 10 wt.% yield of gasoline range hydrocarbons using a pilot plant vortex reactor followed by a fixed-bed catalytic cracker. French and Czernik (2010) screened metal-modified zeolite catalysts for catalytic pyrolysis in a system consisting of a tubular pyrolysis reactor and a fixed catalyst bed. Hydrocarbon yield of 16 wt.% was achieved using nickel-substituted HZSM-5. Adam et al. (2006) examined several mesoporous catalysts in a lab-scale fixed bed reactor with similar arrangements of pyrolyzer and catalyst bed as. Increased yields of hydrocarbon and phenol in the organic phase were reported. Williams and Nugranad (2000) pyrolyzed rice husks in a fluidized bed reactor with catalytic conversion of pyrolysis vapors in a downstream HZSM-5 catalyst bed. They found aromatic hydrocarbons increased with increasing catalyst temperature, while bio-oil yield markedly decreased.

To date, no direct comparisons between *in-situ* and *ex-situ* CP have been reported. Such comparisons might help understand the reaction mechanisms for catalytic pyrolysis and improve the design of catalytic pyrolysis systems. The present study conducts experiments on both *in-situ* and *ex-situ* CP using a micro-scale reactor system that consists of two reactors in series that are housed in separate furnaces with independent temperature control. For *in-situ* CP, biomass and catalyst were mixed together in the first (pyrolysis) reactor with the second reactor empty. For *ex-situ* experiments, biomass was loaded in the first (pyrolysis) reactor and zeolite catalyst loaded in the second reactor. Product distributions for the two kinds of CP were compared. The effect of pyrolysis temperature, catalysis temperature, and catalyst loading for *ex-situ* CP were investigated to determine their influence on the yield and composition of aromatics, olefins and other non-condensable gases.

2. Methods

2.1. Materials

Hybrid poplar wood with a particle range of approximately 0.2–3 mm was purchased from Wood Residual Solutions (USA). To eliminate interferences by naturally occurring alkali and alkaline earth metals in the biomass, the wood was washed with acid solution using the method described by Patwardhan et al. (2010). The acid-washed poplar sample was ground using a ball mill to obtain particle size below 200 mesh. Component analysis of the poplar was determined by the methods described in the literature (Sluiter et al., 2011). Cellulose, in the form of microcrystalline powder, was purchased from Sigma Aldrich. Milled wood lignin prepared according to the procedures recommended by Björkman (1956) was used in this study. Results for elemental and compositional analyses of the feedstocks are listed in Table 1.

2.2. Pyrolysis equipment and analytical instrumentation

A Tandem micro-reactor system (Rx-3050 TR, Frontier Laboratories, Japan) was used for the catalytic pyrolysis experiments. A schematic diagram of the system is shown in Fig. 1. It consists of two reactors arranged in tandem, both of which can be independently controlled in the temperature range of 40–900 °C. The inter-

Table 1
Elemental and compositional analyses of feedstocks.

Feedstock	Elemental analysis (wt%)				Composition analysis ^a (wt%)		
	C	H	N	O	Cellulose	Hemicellulose	Lignin
Hybrid Poplar	50.0	6.2	0.1	43.0	45.3	18.2	30.0
Cellulose	44.0	6.7	0.0	53.3	100.0	–	–
Lignin	58.3	6.0	0.1	35.6	–	–	100.0

^a Hybrid poplar analyzed on an air-dry basis. Water, ash, and extractive content are not explicitly measured except by difference.

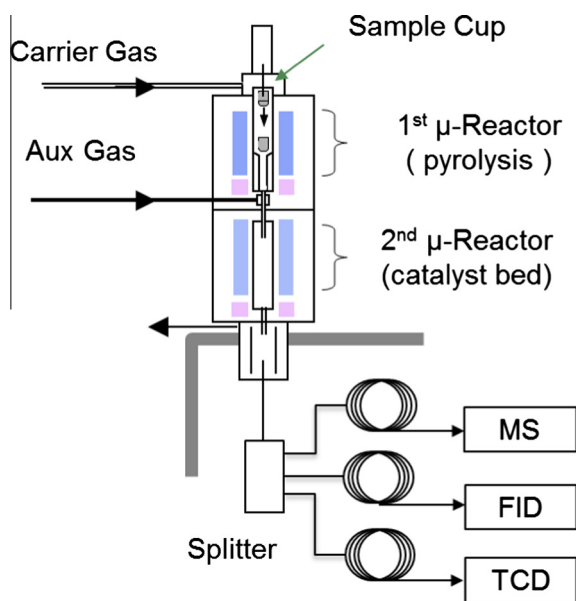


Fig. 1. Schematic diagram of Tandem Micro-Reactor system in this study.

face between the furnace and gas chromatograph (GC) can be independently heated to 100–400 °C. Helium gas was used as carrier gas to sweep the reaction products into a GC for detailed compositional analysis.

We chose commercially available HZSM-5 catalyst (CBV2314 with SiO₂/Al₂O₃ ratio of 23, Zeolyst, USA) for this study. The catalyst was calcined at 550 °C (5 °C/min) for 5 hours in a muffle furnace to activate it prior to use. For *ex-situ* CP, approximately 0.5 mg biomass sample was pyrolyzed in the first reactor and the pyrolysis vapors transported to the second reactor containing catalyst particles of 50–70 mesh size, which was prepared by pelletizing and sieving. Quartz wool was used to support the catalyst particles and prevent solids from exiting the catalyst bed. The temperatures of the pyrolysis and catalysis reactors were controlled independently during *ex-situ* CP experiments. The interface temperature was set to 350 °C to minimize condensation of products. For *in-situ* CP, catalyst was prepared as described above and directly mixed with biomass particles sized to less than 200 mesh using a catalyst-to-biomass weight ratio of 20. Approximately 5 mg of biomass/catalyst mixture was pyrolyzed in the first reactor at the desired pyrolysis temperature. The reactor in the second furnace was empty for these *in-situ* catalytic experiments, with the temperature of the second furnace and the interface held at 350 °C to prevent product condensation. A microbalance (PX6, Mettler Toledo, Swaziland) with sensitivity of 0.001 mg was used to determine the sample weight in this study.

The products were analyzed by a gas chromatograph (GC) (7890A, Agilent Technologies, USA) installed with a three-way splitter that directed the gas stream to three GC columns. The GC oven was programmed for a 3-minute hold at 40 °C then ramped at 10 °C/min to 250 °C, after which temperature was held

constant for 6 minutes. The injector temperature was 250 °C and the total helium flow passing through the reactor was 90 ml/min. Two identical capillary columns, Phenomenex ZB 1701 (60 m × 0.250 mm and 0.250 μm film thickness) were used to separate condensable aromatic hydrocarbons. One 1701 column was connected to a mass spectrometer (MS) (5975C, Agilent Technologies, USA) for compound identification while the other one was connected to a flame ionization detector (FID) for product quantification by calibration with standards. A Porous Layer Open Tubular (PLOT) column (60 m × 0.320 mm) (GS-GasPro, Agilent, USA) connected to a thermal conductivity detector (TCD) was used to measure non-condensable gas (NCG) products (CO, CO₂, CH₄, C₂H₄, C₂H₆, C₃H₆, C₃H₈, and C₄H₈). A standard gas mixture consisting of these NCG compounds in helium (Praxair, USA) was used to calibrate the yield of NCG. Olefins and alkenes ≥ C₅ were either not detected or negligible in this study.

For *ex-situ* CP, the yield of pyrolysis char generated in the first reactor and catalytic coke deposited on the catalyst in the second reactor were analyzed separately. Carbon in the char product and coke were quantified by combustion analysis using an elemental analyzer (vario MICRO cube, Elementar, USA). Because the biomass and catalyst were mixed together for *in-situ* CP, distinguishing between pyrolysis-derived char and catalysis-derived coke was not possible. Thus, yields of total carbonaceous residues in the mixture after reaction, quantified by combustion analysis, were determined.

All measurements including aromatics, NCG, and carbonaceous residues, were performed at least in duplicate to verify the reproducibility of the data. Final product distribution was reported as molar carbon yield, defined as the molar ratio of carbon in a specific product to the carbon in the feedstock. Carbon atom efficiency in producing desired products (aromatics and olefins) was calculated as moles of carbon atoms in these products divided by the moles of carbon atoms in the biomass. Selectivity for aromatics in this study was defined as moles of carbon in a specific aromatic hydrocarbon to total moles of carbon in the aromatic products. Selectivity of olefins was similarly defined. The overall carbon balance was performed for each run, which closed at over 90% in most cases. The unaccounted fraction included large molecular weight compounds unidentified by GC and/or unrecovered char/coke deposited on the walls of the reactors.

3. Results and discussion

3.1. Effect of catalyst loading on *ex-situ* CP

Because zeolite catalysts can rapidly deactivate due to the build-up of coke on the surface of the catalyst, tests were conducted to determine the appropriate catalyst-to-biomass ratio for *ex-situ* CP experiments without needing to replace catalyst between replicated tests. Catalyst loadings of 10 mg, 20 mg and 40 mg in the second reactor were tested for three replications of *ex-situ* CP, each using 0.5 mg biomass in the first (pyrolysis) reactor. These represented initial catalyst-to-biomass ratios of 20, 40, and 80, respectively. Such high catalyst loadings were chosen with

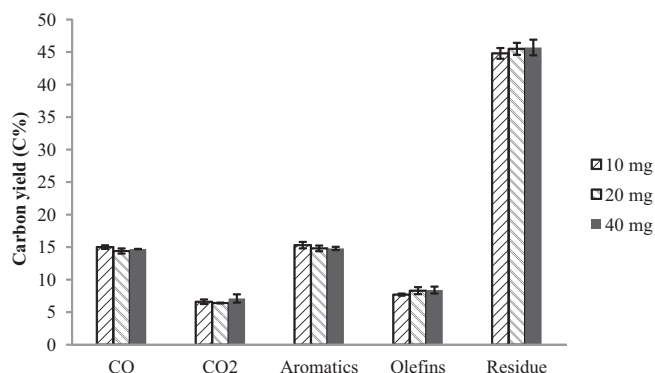


Fig. 2. Effect of catalyst loading on distribution of products for *ex-situ* CP of hybrid poplar (biomass loading: 0.5 mg; pyrolysis temperature: 500 °C; catalysis temperature: 500 °C).

the intention of substantially deoxygenating the pyrolysis vapors to aromatic compounds and olefins. Reaction temperatures for both reactors were kept at 500 °C.

Products distribution from these three catalyst loadings are summarized in Fig. 2. It can be seen that no significant differences in product distributions were observed. Carbon yield of aromatics and olefins were around 15% and 8%, respectively, for all catalyst loadings. Yield of CO, CO₂ and carbonaceous residues were consistently measured around 15%, 7%, and 45%, respectively, for all catalyst loadings. Coke formation in the catalyst bed was consistently at the entrance of the bed, indicating substantial capacity to catalytically convert the vapors for three to four successive replications of *ex-situ* catalysis trials. For subsequent experiments of *ex-situ* CP, catalyst loadings of 10 mg were deemed adequate to obtain reproducible results.

3.2. Effect of pyrolysis temperature on *ex-situ* CP

To investigate the effect of pyrolysis temperature on *ex-situ* CP, catalyst temperature was kept at 500 °C while the pyrolysis temperature was varied between 400 °C and 700 °C. The resulting product distributions are summarized in Table 2.

As shown in Table 2, the carbon yield of olefins for *ex-situ* CP changed only slightly as pyrolysis temperature increased from 400 °C to 700 °C, increasing from 7.1% to 9.9%. Non-catalytic pyrolysis of hybrid poplar at the same four temperatures as shown in Table 2 produced olefin yields of 0.1%, 0.2%, 0.7% and 2.6%. Thus, much of the increase in olefin yields in this temperature range could be ascribed to thermal rather than catalytic effects. Aromatic yield did not change significantly with increasing pyrolysis temperature. Carbon yields of aromatic hydrocarbons were 14.1%, 15.3%, 14.1% and 14.6% for pyrolysis temperatures of 400 °C, 500 °C, 600 °C and 700 °C, respectively. The distribution of aromatic hydrocarbons also remained unchanged at pyrolysis temperatures in the temperature range of 500–700 °C.

The reason for the small pyrolysis temperature effect on aromatic yield may be the result of two counteracting processes during CP. Previous studies have shown that increasing pyrolysis temperature favors formation of light oxygenates, which because of their small size are more readily able to enter the pores of zeolite catalyst to form desirable hydrocarbons (Jae et al., 2011; Patwardhan et al., 2011). On the other hand, increasing pyrolysis temperature is well known to increase the yield of carbon oxides, especially CO as the temperature becomes very high. Non-catalytic pyrolysis of hybrid poplar was performed at temperature of 400 °C, 500 °C, 600 °C and 700 °C. Carbon yield of CO at these temperatures was 1.2%, 2.2%, 5.1% and 11.1%, respectively. Carbon yield of CO₂ over the same temperature range was smaller, but still almost doubled from 3.3% at 400 °C to 6.1% at 700 °C. This large increase in permanent gases as temperature increased would dramatically decrease the concentration of organic vapors, which would be expected to decrease production of hydrocarbons over the zeolite catalyst bed. The simultaneous increase in small organic molecules and non-condensable gases with increasing pyrolysis temperature, however, would mitigate against change in aromatic yield.

As expected, char yield decreased with increasing pyrolysis temperature, which enhanced the decomposition of biomass in the pyrolysis reactor. Carbon yield of pyrolysis char decreased rapidly from 26.5% to 11.1% as the pyrolysis temperature increased from 400 °C to 700 °C. As shown in Table 2, the amount of coke deposited on the catalyst bed was not significantly influenced by pyrolysis temperature. Yields of catalytic coke were around 24% at pyrolysis temperature over the range of 400–600 °C. Changes

Table 2

Effect of pyrolysis temperature on distribution of products for *ex-situ* CP of hybrid poplar (catalysis temperature: 500 °C; biomass loading: 0.5 mg; catalyst loading: 10 mg).

Pyrolysis temperature/°C	400	500	600	700
Overall yield/C%				
CO	13.3 ± 0.06	15.0 ± 0.27	15.5 ± 0.02	19.8 ± 0.10
CO ₂	5.90 ± 0.05	6.60 ± 0.35	6.6 ± 0.25	6.90 ± 0.34
Pyrolysis char	26.5 ± 0.40	18.3 ± 0.09	16.4 ± 0.11	11.1 ± 0.29
Catalytic coke	25.8 ± 1.02	26.5 ± 0.73	23.8 ± 0.48	18.8 ± 0.58
Total carbonaceous residues ^a	52.3 ± 1.42	44.8 ± 0.82	40.2 ± 0.59	29.9 ± 0.87
Aromatic hydrocarbons	14.1 ± 0.55	15.3 ± 0.50	14.1 ± 0.59	14.6 ± 0.23
Olefins	7.10 ± 0.16	7.70 ± 0.16	8.0 ± 0.30	9.90 ± 0.16
Carbon atom efficiency	21.2 ± 0.71	23.0 ± 0.66	23.6 ± 0.53	24.5 ± 0.39
Total carbon balance	93.7 ± 2.24	89.4 ± 2.10	86.9 ± 1.42	85.4 ± 1.72
Aromatic selectivity/%				
Benzene	12.4 ± 0.63	11.7 ± 0.07	12.4 ± 0.10	12.9 ± 0.22
Toluene	41.6 ± 0.81	33.7 ± 0.37	29.5 ± 0.05	29.2 ± 0.46
Xylene	13.3 ± 0.05	19.2 ± 0.69	21.1 ± 0.70	21.6 ± 0.23
C ₉ aromatics ^b	10.7 ± 0.45	9.9 ± 0.71	10.0 ± 0.74	9.70 ± 0.42
C ₁₀₊ aromatics ^c	22.2 ± 1.03	25.8 ± 0.29	27.2 ± 0.19	26.8 ± 0.48
Olefin selectivity				
Ethylene	41.5 ± 0.16	50.5 ± 0.20	52.1 ± 0.92	52.6 ± 0.21
Propene	50.9 ± 0.29	43.7 ± 0.07	41.3 ± 0.36	41.4 ± 0.33
Butene	7.70 ± 0.44	5.90 ± 0.13	6.70 ± 0.56	6.20 ± 0.54

^a Sum of pyrolysis char and catalytic coke.

^b C₉ aromatics include indanes, indenenes, and alkylbenzene.

^c C₁₀₊ aromatics include naphthalenes and higher polyaromatics (≤C₁₅).

Table 3Effect of catalyst temperature on product distributions for *ex-situ* CP of hybrid poplar (pyrolysis temperature: 500 °C, biomass loading: 0.5 mg; catalyst loading: 10 mg).

Catalyst temperature/°C	400	500	600	700
<i>Overall yield/C%</i>				
CO	10.0 ± 0.05	15.0 ± 0.27	16.1 ± 0.08	21.3 ± 0.09
CO ₂	5.80 ± 0.27	6.60 ± 0.35	7.30 ± 0.24	8.30 ± 0.50
Pyrolysis char	18.3 ± 0.09	18.3 ± 0.09	18.3 ± 0.09	18.3 ± 0.09
Catalytic coke	37.1 ± 0.33	26.5 ± 0.73	17.9 ± 0.62	13.8 ± 0.48
Total carbonaceous residues ^a	55.4 ± 0.42	44.8 ± 0.82	36.2 ± 0.71	32.1 ± 0.57
Aromatic hydrocarbons	7.10 ± 0.34	15.3 ± 0.50	19.5 ± 0.09	19.4 ± 0.29
Olefins	2.60 ± 0.23	7.70 ± 0.16	13.6 ± 0.24	17.3 ± 1.04
Carbon atom efficiency/%	9.70 ± 0.57	23.0 ± 0.66	33.1 ± 0.33	36.7 ± 1.33
Total carbon balance	80.9 ± 1.31	89.4 ± 2.10	95.2 ± 1.47	103 ± 2.51
<i>Aromatic selectivity/%</i>				
Benzene	5.90 ± 0.18	11.7 ± 0.07	22.1 ± 0.08	36.8 ± 0.57
Toluene	32.9 ± 1.51	33.7 ± 0.37	37.2 ± 0.29	32.3 ± 0.21
Xylene	20.3 ± 2.84	19.2 ± 0.69	12.7 ± 0.09	8.60 ± 0.01
C ₉ aromatics ^b	13.8 ± 1.56	9.90 ± 0.71	8.70 ± 0.1	7.10 ± 0.53
C ₁₀₊ aromatics ^c	27.6 ± 3.24	25.8 ± 0.29	19.6 ± 0.36	15.4 ± 1.29
<i>Olefin selectivity</i>				
Ethylene	28.8 ± 0.56	50.5 ± 0.20	52.8 ± 0.48	56.8 ± 0.44
Propene	58.3 ± 1.17	43.7 ± 0.07	43.1 ± 0.10	38.2 ± 0.79
Butene	13.0 ± 0.61	5.90 ± 0.13	4.30 ± 0.57	5.20 ± 0.36

^a Sum of pyrolysis char and catalytic coke.^b C₉ aromatics include indanes, indenenes, and alkylbenzene.^c C₁₀₊ aromatics include naphthalenes and higher polyaromatics (\leq C₁₅).

in CO and CO₂ were also insignificant in the pyrolysis temperature range of 400–700 °C, with the exception that CO increased from 15.5% to 19.8% as temperature increased from 600 °C to 700 °C. It is more likely that the increase is ascribed to thermal decomposition in the pyrolysis reactor, as described above.

3.3. Effect of catalysis temperature on *ex-situ* CP

To investigate the effect of catalyst temperature, hybrid poplar was pyrolyzed at 500 °C, while increasing the catalyst temperature from 400 °C to 700 °C. Product distributions are summarized in Table 3.

As shown in Table 3, the yield of CO₂ increased slightly from 5.8% to 8.3% as temperature increased. Yield of CO increased from 10% at 400 °C to 21.3% at 700 °C. This is in accordance with our previous study of CP, which showed that decarbonylation to CO is favored over decarboxylation to CO₂ for catalytic pyrolysis of biomass (Wang et al., 2014). Increasing CO yield correspond to an increase in aromatics and olefins with increasing temperature, which also indicated that catalytic CO generation is mechanistically related to the production aromatics and olefins (Foster et al., 2012; Wang et al., 2014). Yield of catalyst coke fell from 37.2% to 13.8% as catalyst temperature increased from 400 °C to 700 °C. Thus, increasing catalyst temperature improves yields of desired products while reducing coke formation.

Catalyst temperature affected yield of both aromatic and olefins. Total yield of which increased from 9.7% to 36.7% in increasing the catalyst temperature from 400 °C to 700 °C. However, the influence of catalyst temperature was different for the two products. At 400 °C, yield of aromatics was 7.1%, which increased to 15.3% at 500 °C, but remained relatively constant with further increase in temperature. Selectivity for specific aromatic hydrocarbons varied dramatically with temperature. High temperature favored the formation of small aromatics especially benzene. Aromatic selectivity for benzene was only 5.9% at 400 °C increasing to 36.8% at 700 °C. Aromatic selectivity for toluene remained approximately constant at 33%, while selectivity for xylene and higher aromatics decreased significantly. Aromatic selectivity for xylene decreased from 20.3% to 8.6% as temperature increased from 400 °C to 700 °C. Aromatic

selectivity for C₁₀₊ aromatics decreased from 27.6% to 15.4% over the same temperature range. One possible reason is that higher temperatures favor desorption of products from zeolite before further reaction can form larger aromatics. Additionally, high temperatures enhanced the dealkylation of alkylbenzenes, which may also account for the selectivity toward smaller aromatics especially benzene (Al-Khattaf, 2006).

Compared with aromatics, yield of olefins was more highly influenced by catalyst temperature. Yield of olefins at 400 °C was only 2.6% but increased almost five-fold to 17.3% as temperature increased to 700 °C. Olefin yield increased monotonously from 13.6% to 17.3% as catalyst temperature increased from 600 °C to 700 °C in contrast to the constancy for aromatic yield. Selectivity of olefins was also affected by catalyst temperature. This temperature behavior is similar to that observed by Cheng and Huber (2011) who also saw a shift in selectivity from aromatics to olefins as catalyst temperature increased in a study on furan conversion over HZSM-5. The different yield responses of olefins and aromatics to changes in catalyst temperature suggest different reaction pathways for these two products. Also notable was a shift in olefin selectivity from propene to ethylene as catalyst temperature increased, with ethylene selectivity increasing from 28.8% to 56.8% as temperature increased from 400 °C to 700 °C.

The theory of indirect hydrocarbon pools in zeolites, originally formulated to explain the methanol to gasoline process via zeolite catalysts, has also found application in explaining catalytic pyrolysis of biomass (Dahl and Kolboe, 1994). However, previous studies of catalytic pyrolysis focused on production of aromatics, overlooking the significant production of olefins. Recent studies on the hydrocarbon pool mechanism have led to the concept of dual catalytic cycles (Björger et al., 2007; Ilias and Bhan, 2012a,b), which helps explain the different effect of temperature on aromatics and olefins production observed in the present work. The dual-cycle mechanism is introduced for biomass catalytic pyrolysis and depicted in Fig. 3. During pyrolysis biomass is thermally decomposed into vaporous oxygenates including furanic compounds, acids, and phenols. As these biomass-derived oxygenates diffuse into pores of zeolite, two catalytic cycles operate in competition with each other: the olefin cycle involving methylation/

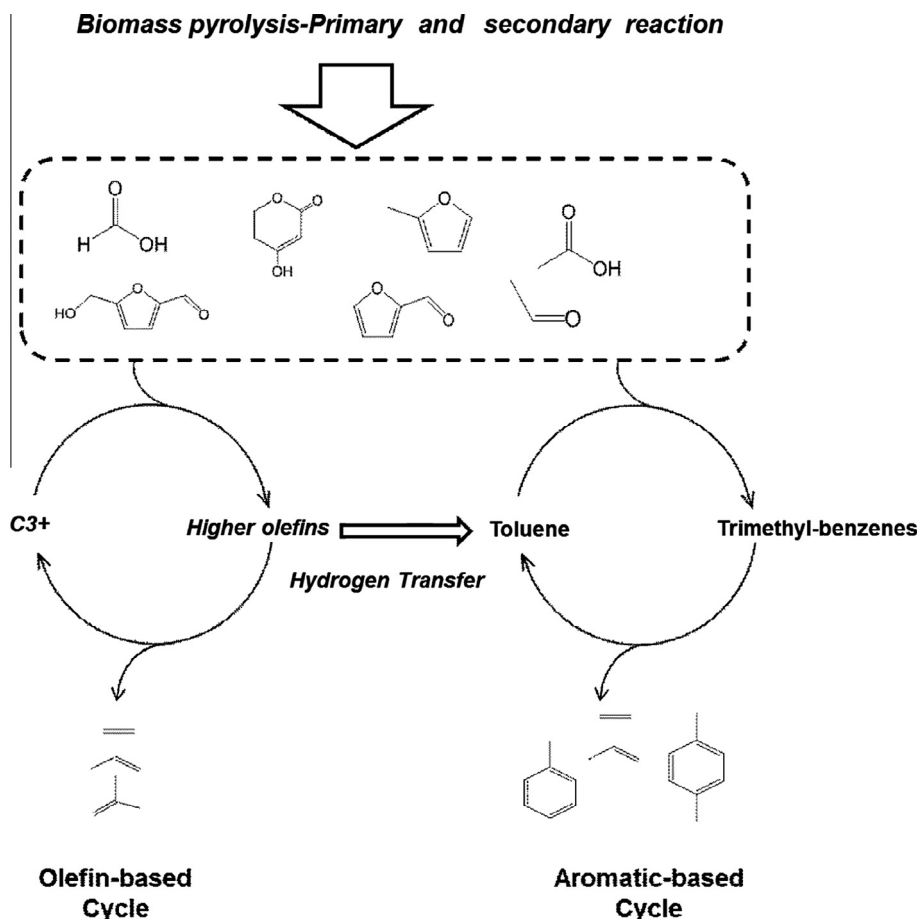


Fig. 3. Dual olefin-based and aromatic-based cycles for catalytic pyrolysis of biomass over HZSM-5.

cracking of olefins and the aromatics-based cycle involving methylation/dealkylation of polymethylbenzenes (Björge et al., 2007; Ilias and Bhan, 2012a; Sun, 2013).

A previous study on methanol to olefin (MTO) reported the activation energy for olefin formation was 93 kJ/mol, while that for hydrogen transfer to aromatics formation was only 9 kJ/mol. (Sun, 2013) Increasing reaction temperature would significantly enhance the rate of olefin formation compared to aromatics. At low temperatures, the aromatic carbon pool would dominate while the olefin carbon pool would dominate at high temperatures. This is consistent with the observations of this study, which found that increasing catalyst temperature had a greater effect on yields of olefins than aromatics.

Notice that both the aromatic-based and olefin-based cycles in the dual cycle mechanism contribute to olefin production, with the aromatic-based cycle more selective for ethylene production. (Ilias and Bhan, 2012b; Sun, 2013) Increasing temperature enhances dealkylation reactions to form ethylene in the aromatic based cycle. Although the olefin-based cycle is less selective for ethylene formation, selectivity for ethylene, which is thermodynamically favored, increased with increasing temperature (Sun, 2013).

3.4. Comparison of ex-situ and in-situ catalytic pyrolysis

To compare *in-situ* and *ex-situ* CP, both kinds of CP were performed in the tandem reactor system. The first (pyrolysis) reactor was held at 700 °C for both kinds of CP while the second reactor was held at 700 °C when loaded with catalyst for *ex situ* CP and at 350 °C when empty for *in situ* CP (to prevent product condensa-

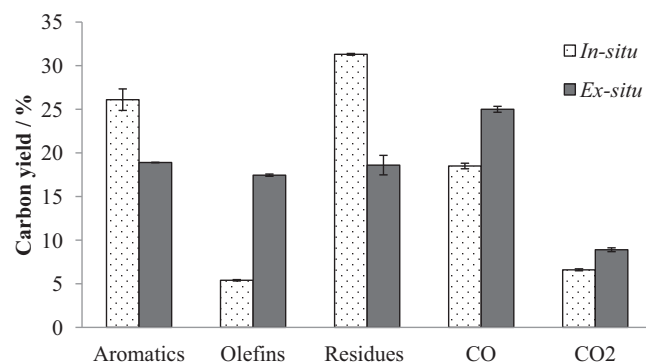


Fig. 4. Distribution of products for *ex-situ* and *in-situ* CP of hybrid poplar (Pyrolysis temperature: 700 °C; catalyst temperature for *ex-situ* CP: 700 °C; catalyst-to biomass ratio = 20; residues: sum of pyrolysis char and catalytic coke).

tion). Product distributions for both kinds of pyrolysis are summarized in Fig. 4. *In-situ* CP generated strikingly more aromatic hydrocarbons than did *ex-situ* CP. At 700 °C, carbon yield of aromatics for *in-situ* CP was 26.1% compared to only 18.5% for *ex-situ* CP. In comparison, olefin yield from *ex-situ* CP was as high as 17.4%, which was three times higher than for *in-situ* CP at 700 °C. Thus, for *ex-situ* CP olefins are preferentially produced compared to aromatics. *In-situ* and *ex-situ* CP experiments were also performed with milled wood lignin and cellulose, product distributions from which are summarized in Table S1. It also showed that *ex-situ* CP produced significantly more olefins and less aromatic compounds. A

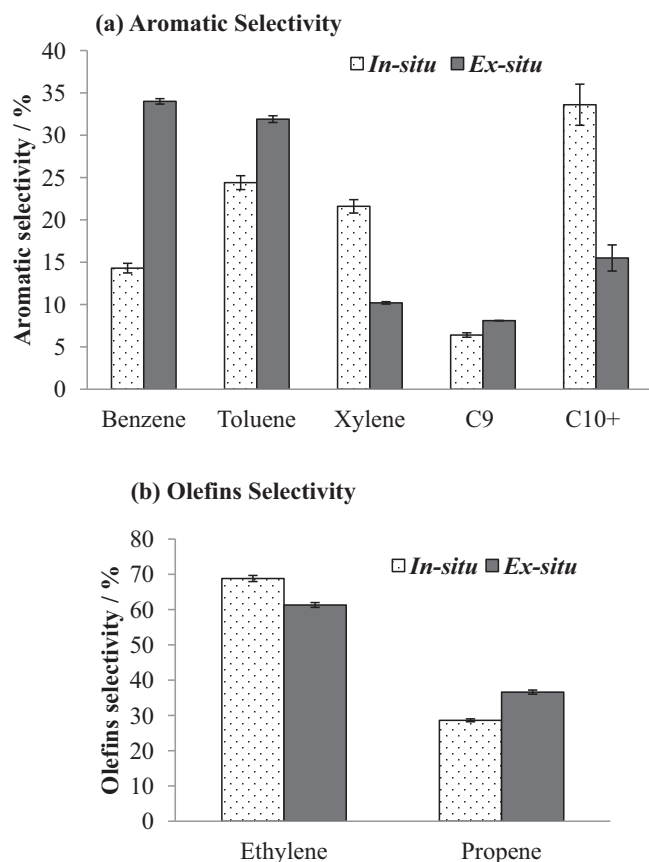


Fig. 5. Product selectivity for *in-situ* and *ex-situ* CP of hybrid poplar (a): Aromatic selectivity (b): Olefin selectivity (Pyrolysis temperature: 700 °C; Catalyst temperature for *ex-situ* CP: 700 °C; catalyst-to-biomass ratio = 20; C₉ aromatics include indanes, indenenes, and alkylbenzene; C₁₀₊ aromatics include naphthalenes and higher polyaromatics).

recent study by Carlson et al. (2011) on the conversion of furan over HZSM-5 showed that higher yield of aromatics were obtained for *in-situ* catalysis using with a pyroprobe instrument compared to *ex-situ* pyrolysis in a fixed bed reactor.

Since aromatics and olefins are two important products from catalytic pyrolysis, detailed distributions of these two types of products are summarized in Fig 5(a) and (b). Aromatic selectivity was distinct for these two types of pyrolysis. Selectivity of monocyclic aromatics such as benzene and toluene for *ex-situ* CP was higher than for *in-situ* CP, while *in-situ* CP generated more naphthalenes and higher polyaromatics. At 700 °C, aromatic selectivity of benzene and toluene were 34% and 31.9%, respectively, for *ex-situ* CP compared to 14.3% and 24.4%, respectively, for *in-situ* CP. More rapid desorption of aromatic hydrocarbon products from the acid sites of the zeolite catalyst during *ex-situ* CP might explain the lower yields of polyaromatics compared to *in-situ* CP. Olefins formed from both types of catalytic pyrolysis were predominantly ethylene and propene. Selectivity of propene for *ex-situ* CP was higher than for *in-situ* CP.

Differences in yields of olefins and aromatics for *in-situ* and *ex-situ* CP are statistically significant. A possible explanation is differences in gas flow for the two arrangements of catalysts. For *in-situ* CP, biomass was directly mixed with the catalyst; thus, the catalyst was exposed to a concentrated stream of pyrolysis vapors. For *ex-situ* CP, the vapors released from the pyrolyzing biomass were mixed with sweep gas before being transported through the catalyst bed; thus, the pyrolysis vapors were diluted and had a shorter contact time with the catalyst compared to *in-situ* CP. Accordingly,

in-situ CP provided more opportunity for small olefins to oligomerize to larger aromatic compounds at acid sites within the zeolite pores. Moreover, the resulting monocyclic aromatics may more readily methylate and oligomerize to larger aromatics during *in-situ* CP as a result of suppressed mass transfer (Ilias and Bhan, 2012b; Sun, 2013). Since the aromatic-based cycle is more selective for ethylene production (Ilias and Bhan, 2012a,b), ethylene selectivity for *in-situ* CP would be expected to be higher than for *ex-situ* CP, as observed in this study.

It should be noted that the large mass of catalyst mixed with biomass for *in-situ* CP would substantially slow the heating rate of biomass during pyrolysis, likely suppressing olefin-based cycle, as discussed in Section 3.3. In contrast, *ex-situ* CP occurred at constant set-point temperature because the catalyst is preheated in a separate reactor from pyrolysis, favoring olefin formation.

The yield of carbonaceous residues for *ex-situ* CP was 18.6%, which was much lower than the 31.3% observed for *in-situ* CP. For *in-situ* CP, lower mass transfer rates as previously described would enhance coke-forming reactions, which would explain the higher yield of residue. For *ex-situ* CP, large amounts of carbon were deposited as pyrolysis char. At pyrolysis temperature of 700 °C, thermal char yield and catalytic coke yield were 11.1% and 7.5% respectively. This suggests that *ex-situ* CP has the potential to reduce the rate of catalyst regeneration. Furthermore, pyrolysis char can be separated as a by-product, which has potential as carbon sequestration agent and soil amendment (Brewer et al., 2009).

4. Conclusions

The effect of catalyst loading, pyrolysis temperature, and catalyst temperature on production of aromatics and olefins for *ex-situ* CP of hybrid poplar were investigated. The results indicate that pyrolysis temperature had negligible effect on catalytic pyrolysis despite the fact that more small oxygenates are formed at high pyrolysis temperature. On the other hand, product distribution highly depended on catalyst temperature. Product selectivity shifted from aromatics to olefins as catalyst temperature increased. A dual catalytic reaction cycle mechanism was introduced to explain these differences. *In-situ* and *ex-situ* CP were compared using identical reaction conditions. The carbon atom efficiency obtained from *ex-situ* CP was 35.9% when both pyrolysis and catalyst temperatures were 700 °C. Yields of olefins and aromatics for *ex-situ* CP of hybrid poplar were 17.4% and 18.5%, respectively. In comparison, *in-situ* CP produced significantly more aromatics and less olefins with yields of 26.1% and 5.4%, respectively. Selectivity of monocyclic aromatics such as benzene and toluene for *ex-situ* CP was higher than for *in-situ* CP, while *in-situ* CP generated more naphthalenes and other polyaromatics. Differences yields of aromatics and olefins for *in-situ* and *ex-situ* CP are explained by differences in gas flow and heat transfer for the two kinds of CP. The remarkably high olefin yield from *ex-situ* CP suggests the possibility of exploiting the process to preferentially obtain olefins from biomass.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.biortech.2014.09.097>.

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